403 771

63-3-4

OFFICE OF NAVAL RESEARCH

Contract Nonr-2121(16)

Project NR 052-415

FINAL REPORT - PART II
(Final Summary)

TRACER STUDIES ON THE OXIDATION OF UO_2 IN

ACIDIC AQUEOUS SOLUTION

by

John B. Hunt and Henry Taube

The University of Chicago

Department of Chemistry

Chicago 37, Illinois

January 22, 1963

Some experiments were done on the oxidation of UO_2 in acidic solution. Since UO_2^{++} has been shown not to undergo rapid exchange of oxygen with the solvent at least when the concentration of U(V) is kept low, an interesting tracer experiment is possible in this system which is relevant to the question: to what extent is UO_2-oxygen retained in the UO_2^{++} which is formed?

Our investigation is by no means complete, nor are our results entirely satisfactory, but they are suggestive of some interesting effects and seem worth reviewing in their present form. The difficulty which limited our work appeared in the isotope analysis of the UO_2^{++}. Although a variety of blank experiments encouraged our hope that the method used by Gordon and Taube[1] would work in our systems, the results obtained when analysis was done on UO_2^{++} produced in a reaction were somewhat erratic.

1. Qualitative Observations Concerning Rates

The experimental data allow only qualitative comparisons of the rates at which various oxidizing agents transform UO_2 to UO_2^{++}. The oxidation of UO_2 by trisdipyridyliron(III) and trisorthophenanthrolineiron(III) ions in 1 $\underline{M}$ HCl is extremely rapid, the reduction of 0.1 $\underline{M}$ solutions of these ions by excess UO_2 being complete within about 1 minute after stirring is commenced at room temperature.[*] The oxidation of UO_2 by Ce(IV) and Ag(I) is rapid.

---

[1] G. Gordon and H. Taube, J. Inorg. & Nuclear Chem., <u>16</u>, 272 (1961).

[*] The surface area of the oxide used in these experiments was about 4 meters^2/g..

Bromate and peroxydisulphate solutions in 1 $\underline{M}$ HCl are unreactive toward the oxide in the absence of metal ion catalysts. The order of efficiencies for the oxidizing agents tested seems to be:

$$Fe(dipy)_3^{+3} \sim Fe(o\text{-phen})_3^{+3} > Ce(IV) \sim Ag(I) > Tl(III) \sim Br_2(aq) \sim Cl_2(aq).$$
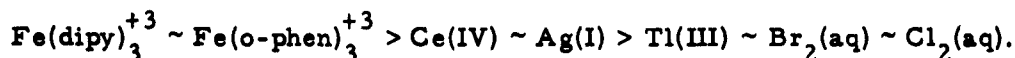
The bulk of our experimental data is concerned with the oxidation of UO_2 by aqueous chlorine. The oxidation of oxides in the composition range $UO_{2.06}$-$UO_{2.14}$ by Cl_2 in HCl solutions is more rapid at lower HCl concentrations. Oxidation by Cl_2 in dilute HCl is less rapid than in dilute $HClO_4$ of comparable acidity. These observations implicate HOCl as the oxidizing species, since the degree of hydrolysis of Cl_2 becomes less as the concentration of HCl increases. Further support for this hypothesis is the fact that oxidation by Cl_2 is more rapid in dilute than in more concentrated $HClO_4$.

2. Oxygen Tracer Experiments

(a) Experimental.--Enriched UO_2 was prepared by the reduction of enriched uranyl chloride in a stream of dry hydrogen at 700°C. This method yielded an oxide which analyzed as $UO_{2.00}$. Oxides of normal isotopic composition were prepared by two methods. The hydrogen reduction of commercial uranous-uranic oxide at 700°C yielded oxides in the composition range $UO_{2.06}$-$UO_{2.08}$. Air ignition (500°C) of ammonium diuranate followed by hydrogen reduction at 800°C yielded an oxide of composition $UO_{2.14}$.

UO_2 samples were analyzed for U(IV) by dissolution in excess ceric sulfate solution followed by back titration of the excess ceric ion with ferrous

ammonium sulfate. Total uranium was determined by titration of a portion of the uranium solution against ceric sulfate after reduction in a Jones reactor.

Water and UO_2 were analyzed for O^{18}-content by the method of Anbar and Guttmann.[2] The O^{18}-content of UO_2^{++} was determined by the method of Gordon and Taube.[1] The latter method involves the precipitation of UO_2^{++} as a ferrocyanide; the precipitate is coagulated with acetone, separated by filtration, vacuum dried, and analyzed for O^{18} by the Anbar-Guttmann technique. It was discovered that uranyl ferrocyanide from some experiments in which aqueous chlorine was the oxidizing agent contained oxygen derived from acetone. Consequently, acetonitrile was used in place of acetone in many of the later experiments.

Except where otherwise indicated, the tracer experiments were carried out in vessels open to the atmosphere and at the ambient temperature. The reaction mixture was agitated by means of a magnetic stirrer. At the end of an experiment any UO_2 remaining was removed by filtration, the excess oxidizing agent removed as described below, and uranyl ferrocyanide was precipitated as outlined above.

It was not necessary to remove excess Tl(III) from uranyl solutions prior to the precipitation of uranyl ferrocyanide. Tl(III) does not interfere with the O^{18} analysis of UO_2^{++} when precipitation is accomplished with deficient ferrocyanide, as shown by the data of Table 9. Excess chlorine was removed either by extraction with CCl_4 or by bubbling nitrogen through the

---

[2] M. Anbar and S. Guttmann, J. Appl. Rad. Isotopes, 5, 233 (1959).

solution for one hour. Bromine was removed by CCl_4 extraction. Dichromate was removed by adsorption on a Dowex-1 column. Ag^+ was precipitated as AgCl. Ce(IV) was removed by reduction with Cr(III), followed by adsorption of $Cr_2O_7^=$ on a Dowex-1 column. Blank experiments showed that this method of removing excess Ce(IV) induced 6.0 to 6.7% exchange between UO_2^{++} and the solvent.

(b) Results.--Data are presented in Table 1 for blank experiments in which uranyl ion of normal isotopic composition was precipitated from O^{18}-enriched water by the method of Gordon and Taube,[1] using a deficiency of ferrocyanide and acetone as the coagulant. These data show that contamination by the solvent does not exceed 1% when the precipitant is a solution of potassium ferrocyanide. Appreciable contamination is observed when crystalline potassium ferrocyanide is used as the precipitant.

Table 1[a]

Precipitation Blank Experiments Testing for Contamination of
Uranyl Ferrocyanide by Solvent Oxygen

| Experiment | Medium | Mass 46/Mass 44, as CO_2 | | |
		H_2O	UO_2^{++}	Standard
1	1 $\underline{M}$ HCl	0.02010	0.004188	0.004140
2	1 $\underline{M}$ HCl	0.02010	0.004174	0.004140
3[b]	1 $\underline{M}$ HCl	0.02010	0.00519	0.00411

[a]Coagulant: acetone.

[b]Precipitation with crystalline $K_4Fe(CN)_6 \cdot 3H_2O$.

The data of Table 2 show that uranyl ferrocyanide may be precipitated without appreciable contamination from the solvent when less than a stoichiometric amount of ferrocyanide solution is the precipitant and acetonitrile is used as the coagulant. In none of the experiments of Table 2 did contamination

Table 2

Precipitation Blanks Testing for Contamination from the Solvent with Acetonitrile Coagulant

| | | Mass 46/Mass 44, as CO_2 | | |
Experiment	Medium	H_2O	UO_2^{++}	Standard
4	1 $\underline{M}$ HCl	0.0205	0.00428	0.00410
5	0.5 $\underline{M}$ HCl	0.01776	0.00426	0.00416
6	0.5 $\underline{M}$ HCl	0.0116	0.00415	0.00415
7	0.5 $\underline{M}$ HCl	0.0120	0.00411	0.00408
8	0.5 $\underline{M}$ HCl	0.0120	0.00409	0.00406
9	Chlorine water	0.0116	0.00415	0.00415
10	Chlorine water	0.0116	0.00411	0.00408

by the solvent exceed 1%. In experiments 9 and 10 crystals of uranyl nitrate were dissolved in chlorine water, and the solution was allowed to stand for one hour. The solution was then made 0.5 $\underline{M}$ in HCl, and chlorine was removed in a stream of nitrogen prior to the addition of the ferrocyanide solution. In experiment 5 acetonitrile was added to the uranyl solution prior to the addition of the ferrocyanide solution.

The data of Table 3 show that acetone oxygen may be incorporated into uranyl ferrocyanide precipitated from uranyl solutions prepared by oxidation

with aqueous chlorine. Solutions containing uranyl ion in isotopic equilibrium

with the solvent were prepared by the dissolution of uranium metal in HCl

solutions saturated with chlorine.

Table 3

Precipitation Blanks Testing for Contamination by Acetone

Experiment	Sample	Mass 46/Mass 44 as CO_2	
		H_2O	UO_2^{++}
11	1	0.0113[a]	0.00727
	2		0.00732
12	1	0.0117	0.0104
	2		0.00996
13	1	0.0117	0.00908
			0.00945
13a		0.00919	0.00910

[a]Analysis of water substituting quinoline for zinc amalgam gave
46/44 = 0.0112.

• Data are presented in Tables 4-6 for tracer experiments in which

oxide samples of composition $UO_{2.15}$ from a single preparation were

oxidized by aqueous chlorine. "% Retention" is defined as the percentage of

the oxygen found in the uranyl ferrocyanide precipitate which was derived from

the oxide. Where data are presented for more than one sample, the various

samples were from separate precipitations from a single solution. The experi-

ments of Table 5 were conducted in closed vessels containing chlorine gas at

the stated pressure.

Table 4[a]

Oxidation of $UO_{2.15}$ by $HClO_4$ Solutions Saturated with Cl_2

Experiment	Sample	$(HClO_4)$	% Retention
14	-	0.94	43.0
15	-	0.94	39.6
16	-	0.47	46.7
17	-	0.47	48.7
18	1	0.094	53.2
	2	0.094	52.2

[a]Coagulation with acetonitrile.

Table 5[a]

Oxidation of $UO_{2.15}$ by 0.1 $\underline{M}$ HCl Solutions Saturated with Cl_2

Experiment	Sample	Pressure, Atm.	% Retention
19	-	0.5	46.0
20	-	0.5	46.5
21	1	1.0	49.3[b]
	2	1.0	50.7
22[c]	1	1.0	57.7
	2	1.0	57.7
23[c]	-	1.0	51.4
24[c,d]	-	1.0	57.5
25	1	2.0	43.4[b]
	2	2.0	43.8

Table 5--Continued

Experiment	Sample	Pressure, Atm.	% Retention
26	1	2.0	38.4
	2	2.0	47.4[b]
27	1	2.1	42.7
	2	2.1	44.2
28	1	2.0	43.5
	2	2.0	47.7[b]
29	-	2.0	45.7
30	1	2.0	43.7
	2	2.0	47.8

[a]Coagulation with acetonitrile, except when otherwise specified.

[b]Coagulation with acetone.   [c]Chlorine water with no added acid.

[d]At 0°C.

Table 6

Oxidation of $UO_{2.14}$ by 1 $\underline{M}$ HCl Saturated with Cl_2

Experiment	Sample	% Retention
31[a]	-	34.6[c]
32[a]	-	33.9[c]
33	1	41.8[c]
	2	44.3[c]
	3	40.2[b]

[a]Carried out simultaneously in separate vessels.

[b]Coagulation with acetone.   [c]Coagulation with acetonitrile.

In Table 7 data are presented for experiments in which samples from a single oxide preparation were oxidized by Cl_2-saturated dilute HCl. Acetone was used as a coagulant, and ionic strength was adjusted with NaCl.

Table 7

Oxidation of $UO_{2.06}$ with Cl_2 in Dilute HCl at $\mu = 2.0$

Experiment	(HCl)	% Retention
34	1.92	52.3
35	0.96	50.5
36	0.48	46.3
37	0.096	42.7
38	0.0096	43.3

Oxidation of the oxide of Table 7 with Br_2-saturated 0.1 $\underline{M}$ HCl indicated 44% retention of oxygen. Oxidation of a sample of this same oxide in 0.48 $\underline{M}$ HCl saturated with Cl_2, gave 48% retention, using CH_3CN as the coagulant.

Data are presented in Table 8 for experiments in which enriched UO_2 was oxidized with a variety of oxidizing agents dissolved in water of normal isotopic composition. Acetone was used as the coagulant in all of these experiments.

Table 8

Oxidation of Enriched UO_2 with Various Oxidizing Agents
in Normal Water

Experiment	Oxidizing Agent	Oxide Composition	% Retention
39	0.05 $\underline{M}$ Ce(IV) in 1.1 $\underline{M}$ HClO$_4$	$UO_{2.00}$	< 1
40	0.05 $\underline{M}$ Ce(IV) in 1.1 $\underline{M}$ HClO$_4$	$UO_{2.06}$	5.0
41	0.05 $\underline{M}$ Ce(IV) in 1.1 $\underline{M}$ HClO$_4$, satd. with Cl$_2$	$UO_{2.06}$	16.8
42	"	$UO_{2.06}$	17.5
43	"	$UO_{2.07}$	15.5
44	0.5 $\underline{M}$ Tl(III) in 1 $\underline{M}$ HCl	$UO_{2.01}$	4.7
45	0.5 $\underline{M}$ Tl(III) 0.5 $\underline{M}$ HCl	$UO_{2.01}$	5.1
46	0.5 $\underline{M}$ Tl(III) in 0.1 $\underline{M}$ HCl	$UO_{2.01}$	11.2
47	1.0 $\underline{M}$ TlCl$_3$ in 0.1 $\underline{M}$ HCl	$UO_{2.01}$	10.2
48	1.4 $\underline{M}$ TlCl$_3$ in 0.1 $\underline{M}$ HCl	$UO_{2.01}$	10.0
49	0.95 $\underline{M}$ Na$_2$Cr$_2$O$_7$ in 0.9 $\underline{M}$ HCl	$UO_{2.01}$	27
50	0.4 $\underline{M}$ K$_2$Cr$_2$O$_7$ in 0.9 $\underline{M}$ HCl	--	42
51[a]	0.5 $\underline{M}$ K$_2$Cr$_2$O$_7$ in 0.9 $\underline{M}$ HCl	--	39.4
52[a]	0.1 $\underline{M}$ HCl, satd. with Cl$_2$	$UO_{2.00}$	12

[a]Composition of oxide unknown. Prepared by a method which yielded nearly stoichiometric UO_2.
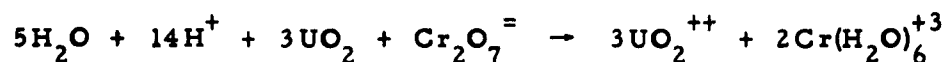
Table 9[a]

Precipitation of Uranyl Ferrocyanide in Presence of Tl(III)

Substance	Mass 46/Mass 44 as CO_2
H_2O	0.0201
Standard CO_2	0.00414
UO_2^{++}	0.00429

[a]$(TlCl_3) = 1.0 \underline{M}$, $(HCl) = 1.0 \underline{M}$, $(UO_2^{++}) = 0.1 \underline{M}$.

The data of Table 10 are from experiments designed to determine whether oxygen may be transferred from UO_2 to chromium in the reaction:

$$5H_2O + 14H^+ + 3UO_2 + Cr_2O_7^= \rightarrow 3UO_2^{++} + 2Cr(H_2O)_6^{+3}$$

In these experiments enriched UO_2 (probably very nearly stoichiometric) was the only source of enriched oxygen. Isotopic analysis of the coordinated water of $Cr(H_2O)_6^{+3}$ was by the method of Hunt and Plane.[3] The data have not been corrected for fractionation effects.

Table 10

Transfer of Oxygen to Chromium in the Oxidation of UO_2 by $Cr_2O_7^=$

Experiment	Oxidizing Agent	O Atoms Transferred/Cr
53	$0.4 \underline{M} K_2Cr_2O_7$ in $1 \underline{M}$ HCl	0.15
54	"	0.04
55	"	< 0.02
56	$1.0 \underline{M} Na_2Cr_2O_7$ in $1 \underline{M}$ HCl	< 0.03

[3]J. P. Hunt and R. A. Plane, J. Am. Chem. Soc., <u>79</u>, 3343 (1957).

Discussion

In spite of the limitations of the data, certain conclusions can be drawn. Since CH_3CN contains no oxygen, the only oxygen-containing contaminant which can be present in the uranyl ferrocyanide coagulated by it is solvent oxygen. Thus, the results obtained with CH_3CN as coagulant set a lower limit on the retention of oxygen in the process

$$UO_2 \rightarrow UO_2^{++} + 2e.$$

This retention is as high as 58% in some experiments (cf. 22 and 24 of Table 5). The retention does apparently vary with oxidation conditions, but no significant pattern seems to emerge from the data. Thus note that whereas the data of Table 4 suggest that the retention increases as the acidity decreases (and this is supported by comparing the data of Table 6 with those of Table 5), the data of Table 7 obtained using a different sample of UO_2 show an opposite trend.

The enriched samples (Table 8) indicate very little retention. Here again, since now UO_2 was enriched in O^{18} and the acetone used as coagulant was of normal isotopic composition, the values recorded are probably lower limits on the actual retention. But it seems entirely likely that the sample of UO_2 in question here, even making allowance for incorporation of acetone oxygen in the uranyl ferrocyanide precipitate, actually behaves quite differently from those prepared in a different way and used in getting the other data.

UO$_2$ has a fluorite structure, with 8 oxygens arranged at the corners of a cube around a uranium in the cube center. With the difference in structure between UO$_2$ on the one hand and UO$_2^{++}$ on the other, it is remarkable that the retention of oxygen on oxidation can be as high as 60%. We are interested in the cause of the defect from 100%: Is it inherent in the process, connected perhaps with the difficulty of extracting linear UO$_2$ units from the UO$_2$ lattice, or is it caused by surface exchange competing with oxidation, or perhaps by UO$_2^{++}$-H$_2$O exchange catalyzed by UO$_2^{+}$? A systematic variation of concentration of oxidizing agent as was attempted in securing the data reported in Table 5 in principle could lead to a distinction between the various hypotheses. But when different samples of UO$_2$ show such remarkably different behavior as we have observed, it is important to learn the cause of this variation before going further. Both studies must wait on an improved method of isotopic analysis, and an effort is being made by one of us (J. B. H.) to define the conditions for successful isotopic assay of UO$_2^{++}$.